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ENERGY-RAY CURABLE RESIN COMPOSITION
[Enerugisen Kokasei Jushi Soseibutsu]

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1. Title

Energy-Ray Curable Resin Composition

2. Claims

1. An energy-ray curable resin composition of the cationic polymerization type essentially comprising:

(a) 60 to 95 parts by weight of one or more kinds of epoxy resins that have one or more epoxy groups in one molecule;

(b) 5 to 40 parts by weight of a thermoplastic saturated polyester resin having an average molecular weight of from 2,500 to 30,000; and

(c) 0.1 to 10 parts by weight, per 100 parts by weight of a mixture of (a) and (b), of a photopolymerization initiator that releases a substance that initiates cationic polymerization when exposed to energy rays.

2. The energy-ray curable resin composition of the cationic polymerization type stated in Claim 1, wherein the component (a), that is, epoxy resins, comprises 20 to 95 % by weight of an alicyclic epoxy resin that has epoxy groups on the alicyclic ring.

3. The energy-ray curable resin composition of the cationic polymerization type stated in Claim 2, wherein the component (a), that is, epoxy resins, comprises 50 to 90 % by weight of an alicyclic epoxy resin that has epoxy groups on the alicyclic ring.

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4. The energy-ray curable resin composition of the cationic polymerization type stated in any of Claims 1 through 3, wherein the average molecular weight of the component (b), that is, a thermoplastic saturated polyester resin, is in the range of from 5,000 to 25,000.

3. Detailed Description of the Invention

The present invention pertains to an energy-ray curable resin composition of the cationic polymerization type. More specifically, it pertains to an energy-ray curable resin composition of the cationic polymerization type that yields strong coating films that exhibit excellent adhesion, flexibility, impact resistance, and the like owing to the fact that the composition comprises, as the essential components, an epoxy resin, thermoplastic saturated polyester resin, and photopolymerization initiator.

Resin compositions that are curable with energy rays, such as ultraviolet rays, electron rays, or the like, have attracted attention /124 from the standpoint of energy conservation, resource conservation, space saving, measures against pollution, and so forth, and research and development concerning these compositions are being actively carried out in the field of inks, coating materials, and varnishes. Along with this, demand for improved coating-film performance is increasing, and, in the field of coating materials, there is a need for energy-ray curable resin compositions that have coating-film performance that is equal or superior to that of conventional solvent-

type coating materials, but no satisfactory compositions have been obtained yet.

The present inventors conducted various studies on energy-ray curable resin compositions so as to produce an energy-ray curable resin composition of the cationic polymerization type that yields strong coating films that exhibit good adhesion to base materials and flexibility and, as a result, learned that an epoxy resin composition that contains a thermoplastic saturated polyester resin yields excellent cured coating films. Based on this finding, the present invention was achieved.

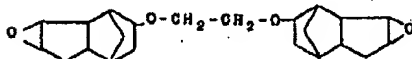
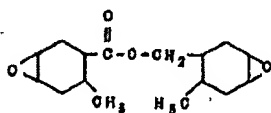
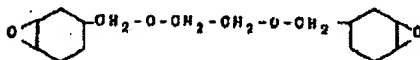
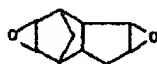
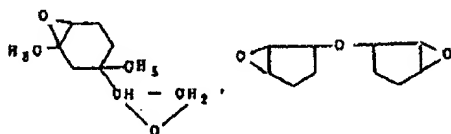
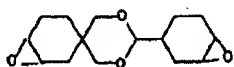
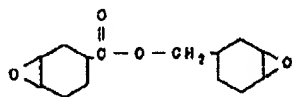
The objective of the present invention is to provide an energy-ray curable resin composition of the cationic polymerization type that yields strong coating films that exhibit excellent coating-film properties, in particular, excellent adhesion to various types of base materials, flexibility, impact resistance, and durability. More specifically, the objective of the present invention is to provide an energy-ray curable resin composition of the cationic polymerization type that is especially suitable for varnishes, coating materials, ink vehicles, covering agents, and so forth.

The present invention's energy-ray curable resin composition of the cationic polymerization type essentially comprises: (a) 60 to 95 parts by weight of one or more kinds of epoxy resins that have one or more epoxy groups in one molecule; (b) 5 to 40 parts by weight of a thermoplastic saturated polyester resin having an average molecular

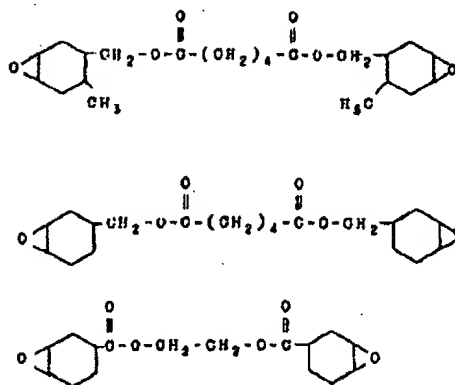
weight of from 2,500 to 30,000; and (c) 0.1 to 10 parts by weight, per 100 parts by weight of a mixture of (a) and (b), of a photopolymerization initiator that releases a substance that initiates cationic polymerization when exposed to energy rays.

The epoxy resins (a) having one or more epoxy groups in one molecule, which are the major constituent of the composition of the present invention, are conventional epoxy resin compositions that polymerize or crosslink when exposed to energy rays in the presence of a photopolymerization initiator and form coating films. Examples of the epoxy resins used in such epoxy resin compositions include conventional aromatic epoxy resins, alicyclic epoxy resins, and aliphatic epoxy resins. Preferable as the aromatic epoxy resins here are polyglycidyl ethers of polyhydric phenols having a minimum of one aromatic nucleus or of their alkylene oxide adducts, and examples thereof include epoxy novolac resins and polyglycidyl ethers that are prepared by the reaction of bisphenol A or its alkylene oxide adducts with epichlorohydrin. Preferable as the alicyclic epoxy resins are polyglycidyl ethers of polyhydric alcohols having a minimum of one alicyclic ring or cyclohexene oxide- or cyclopentene oxide-containing compounds that are obtained by epoxidizing a cyclohexene or cyclopentene ring-containing compound with a suitable oxidizing agent, such as hydrogen peroxide, peracid, or the like. Typical examples of the polyglycidyl ethers of polyhydric alcohols having a minimum of one alicyclic ring include glycidyl ethers that are prepared by the

reaction of hydrogenated bisphenol A or its alkylene oxide adducts with epichlorohydrin. Typical examples of the cyclohexene oxide- or cyclopentene oxide-containing compounds include those represented by the formulas below:



/125



Further, preferable as the aliphatic epoxy resins are polyglycidyl ethers of aliphatic polyhydric alcohols or of their alkylene oxide adducts, polyglycidyl esters of aliphatic long-chain polybasic acids, and homopolymers and copolymers of glycidyl acrylate or glycidyl methacrylate, and typical examples of these include 1,4-butane diol glycidyl ether, 1,6-hexane diol diglycidyl ether, glycerol triglycidyl ether, trimethylolpropane triglycidyl ether, polyethylene glycol diglycidyl ether, polypropylene glycol diglycidyl ether, polyglycidyl ethers of polyether polyols that are obtained by the addition reaction of one or ore kinds of alkylene oxides (such as ethylene oxide and propylene oxide) onto aliphatic polyhydric alcohols, such as ethylene glycol, propylene glycol, glycerol, and the like, and diglycidyl esters of aliphatic long-chain dibasic acids. Furthermore, monoglycidyl ethers of aliphatic higher alcohols; monoglycidyl ethers of phenol, cresol, and butyl phenol or of polyether alcohols obtained by the addition reaction of alkylene oxide onto these; glycidyl esters of higher fatty acids; and the like may also be compounded as a diluent.

As the epoxy resin composition of the present invention, the present invention may use these aromatic epoxy resins, alicyclic epoxy resins, or aliphatic epoxy resins singly or, according to the desired performance, may blend them extensively. However, epoxy resin compositions that are particularly desirable from the standpoint of energy-ray curing properties and adhesion to base materials are those that are mainly composed of alicyclic epoxy resins, in particular, those that contain alicyclic epoxy resins having epoxy groups on the alicyclic ring, like the aforesaid cyclohexene oxide- or cyclopentene oxide-containing compounds, within a range of from 20 to 95 % by weight, preferably from 50 to 90 % by weight [examples of said alicyclic epoxy resins including 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexyl carboxylate, bis (3,4-epoxycyclohexylmethyl) adipate, and the like].

Incidentally, as a constituent of the epoxy resin composition used in the present invention, it is also possible to use cationically polymerizable compounds, such as cyclic ethers, vinyl ethers, lactones, vinyl compounds, and the like, concomitantly with the aforesaid epoxy resins.

The thermoplastic saturated polyester resin having an average /126 molecular weight of from 2,500 to 30,000, which is another essential constituent of the present invention's energy-ray curable resin composition of the cationic polymerization type, is a linear saturated polyester resin having thermoplasticity that is obtained by the

reaction of an organic acid or ester thereof and an alcohol. Examples of the organic acid that is used as the raw material include adipic acid, isophthalic acid, terephthalic acid, phthalic acid, hydrogenated or chlorinated phthalic acid, sebacic acid, trimellitic acid, fatty acid, dimer acid, and the like. Typical examples of the alcohol used here include diethylene glycol, butylene glycol, ethylene glycol, neopentyl glycol, dipropylene glycol, propylene glycol, polypropylene glycol, polyethylene glycol, and the like.

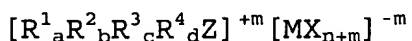
The thermoplastic saturated polyester resin that can be used in the present invention has an average molecular weight within the range of from 2,500 to 30,000, preferably within the range of from 5,000 to 25,000. An average molecular weight of less than 2,500 leads to an insufficient effect of imparting flexibility and adhesion, while an average molecular weight that exceeds 30,000 causes the resin to become less miscible with epoxy resins and so forth and also leads to an insufficient adhesion-improvement effect.

As commercially available thermoplastic saturated polyester resins that are useful in the present invention, there are products of the Toyobo Vylon (a trade name) series (available from Toyo Boseki Co.)--for example, Vylon 103, 200, 300, 500, 560, 600, and 630 and Vylon GK 130--and products of the Vitel (a trade name) series (available from Goodyear Co.)--for example, Vitel PE-200, 207, and the like.

These thermoplastic polyester resins as an essential constituent can be compounded in a widely varying quantity according to the required performance, but, generally speaking, it is suitable to contain them within a range of from 5 to 40 parts by weight per 100 parts by weight of the resin content of the composition of the present invention. A quantity that is less than 5 parts by weight does not yield any effect of blending them, and a quantity exceeding 40 parts by weight causes the viscosity of the composition of the present invention to increase considerably and also gives rise to a tendency for the performance of the energy-ray curable composition proper to deteriorate. A particularly desirable compounding amount is from 5 to 30 parts by weight.

Among these thermoplastic saturated polyester resins, those that have hydroxyl groups or carboxyl groups at the terminals of their molecular chains are particularly effective for improving adhesion.

Meanwhile, the photopolymerization initiator used in the present invention, which releases a substance that initiates cationic polymerization when exposed to energy rays, is not specifically limited, but especially preferable is a group of onium double salts that release Lewis acids capable of initiating polymerization when exposed to radiation. This type of photopolymerization initiator is basically represented by the following general formula:



[wherein the cation is an onium; Z is N≡N, S, Se, Te, P, As, Sb, Bi, O, or a halogen atom (such as I, Br, or Cl); R¹, R², R³, and R⁴ may be identical or different from one another and are organic groups; a, b, c, and d are each an integer of 0 to 3, with the proviso that the sum of a, b, c, and d is equal to the valence of Z; M is a central atom of the halide complex and is a metal or metalloid, such as B, P, As, Sb, Fe, Sn, Bi, Al, Ca, In, Ti, Zn, Sc, V, Cr, Mn, Co, or the like; X is a halogen atom; m is the net charge of the halide complex ions; and n is the number of the halogen atoms in the halide complex ions.]

Such photopolymerization initiators are commonly known. For example, diazonium compounds, in which Z is N≡N, are disclosed in U.S. Pat. No. 3,708,296, No. 3,949,143, No. 3,794,576, and so forth. Other onium-based photopolymerization initiators are disclosed in Belgian Pat. No. 828,841 and No. 828,669, French Pat. No. 2,270,269, and so forth.

The aforesaid diazonium compounds can be obtained by the methods described in the aforesaid U.S. Pat. No. 3,708,296, No. 3,949,143, and so forth. The compounds in which Z is S, Se, or Te can be prepared by, for example, the method described in J. A. C. S., 91, 145 (1969) by J. Knapczyk, et al., the method described in J. Organic Chemistry, 35, No. 8, 2532 (1970) by A. L. Maycock, et al., the method described in Bul. /127 Soc. Chim. Belg., 73, 546 (1964) by Goethals, et al., and the method described in J. A. C. S., 51, 3387 (1929) by H. M. Leicester, et al. Typical onium salts having P, N, As, Sb, or Bi as Z can be prepared by

the method described in Methoden der Organischen Chemie, 11/12, 591-640 (1958) by J. Goerdeler or the method described in the same journal, 12/1, 79-112 (1963) by K. Sasse. Typical onium salts having a halogen atom as Z can be prepared by, for example, the method described in Dokl. Akad. Nauk., SSSR, 163, 383 (1965) by O. A. Ptitsyna, et al. or the method described in J. A. C. S., 75, 2705 (1953) by M. Drexler, et al. The term "onium salts" used herein encompasses pyrylium salts, such as thiopyrylium and the like, described in U.S. Pat. No. 4,139,655 and oxonium salts, such as aryloxysulfoxonium salt and the like, described in JP-A-S56-8428.

Examples of other compounds that can be used for initiating epoxide polymerization include organic halogen compounds, such as iodoform, α,α -dibromoparaxylene, bromoform, carbon tetrabromide, hexachloroparaxylene, other kinds of catalysts described in U.S. Pat. No. 3,895,954, bis(perfluoroalkylsulfonyl)methane salts, and diazonium salts of sulfonyl methane and the like that are described in U.S. Pat. No. 3,586,616, German Pat. No. 2,419,274, and so forth.

These photopolymerization initiators are compounded in an appropriate quantity according to the required cure rate and the curing method employed. Generally speaking, the compounded amount is preferably from 0.1 to 10 parts by weight per 100 parts by weight of the resin content of the curable composition of the present invention.

For the purpose of improving the characteristics of coating materials or coating films, the energy-ray curable resin composition

of the present invention may further incorporate, to an extent that does not adversely affect the effects of the present invention, olefin resins other than the aforesaid cationically polymerizable substances, acrylic resins, petroleum resins, alkyd resins, polyether compounds, polyether polyol compounds, vinyl acetate resins, vinyl chloride resins, butyral resins, rubber resins, vinyl alcohol resins, acid anhydride-based epoxy resin curing agents, pigments, dyes, and various kinds of coating-material additives.

Furthermore, as proposed in U.S. Pat. No. 4,156,035, by incorporating an acrylate or methacrylate compound and a carbonyl photosensitizer or the like into the cationically polymerizable resin composition used in the present invention, it is also possible to improve coating-film performance and curing properties.

The energy-ray curable resin composition of the present invention can be applied to the surface of base materials by an ordinary application method, such as roll coating, gravure coating, gravure offset coating, flow coating, screen printing, spraying, dipping, or the like. In the application step, for the purpose of improving coatability and adhesion to base materials, it is possible to subject the surface of a base material to a pretreatment, such as an alcohol treatment, corona discharge treatment, or the like, and subsequently to apply the resin composition, or it is possible to add an organic solvent to said resin composition to an extent that does not cause any adverse effects, such as performance deterioration and the like, and

then to apply the resulting resin composition. The thickness of the cured coating film should be determined based on the performance required of each base material, but a thickness in a range of from 0.1 to 20 μ or thereabouts is adequate, and a preferable range is from 3 to 10 μ or thereabouts. As the energy rays for forming the curable resin composition of the present invention that has been applied to various kinds of base materials into cured coating films, there are ultraviolet rays, electron rays, radioactive rays, and the like. Among these, the use of ultraviolet irradiation is the most desirable method from the standpoint of practical use. Further, the film formation of the curable composition of the present invention can be effectively promoted by applying the composition to a base material after or while the base material is heat-treated or by applying the curable composition to a base material and subsequently performing the heat treatment and energy-ray irradiation concurrently. In the step of applying said composition, it is also possible to use an organic solvent for viscosity adjustment to an extent that does not cause any adverse effects, such as deterioration of the performance of said energy-ray curable resin composition and so forth.

The energy-ray curable resin composition of the present invention exhibits improved coatability at the time of application and also yields cured coating films that have excellent adhesion to various /128 base materials, flexibility, impact resistance, durability, and so forth due to the fact that it contains, as the essential constituents,

an epoxy resin, thermoplastic saturated polyester resin, and photopolymerization initiator.

That is, the energy-ray curable resin composition of the present invention, after applied to and cured on the surface of various kinds of base materials, can undergo post-processing, such as bending, forming, embossing, laminating, printing, and so forth. Further, after the surface of the cured coating film is subjected to a pretreatment, such as a corona discharge treatment or the like, it is possible to perform a post-process, such as laminating, metal vapor deposition, printing, and the like. The curable composition of the present invention can be used as, for example, protective coating materials, finishing coating materials, covering materials, intermediate coating materials, and primers for various kinds of base materials, including various kinds of plastic films and sheets, such as agricultural-use films and sheets, vinyl chloride decorative films, plastic adhesive films, magnetic tape-use polyester films, vapor deposition-use films and sheets, and so forth, wrapping paper, paper containers, printing paper, such as labeling paper and the like, metal cans, steel sheets, aluminum foil, and the like, and as ink vehicles and so forth.

The following will explain in further detail some representative examples of the energy-ray curable resin composition of the present invention as working examples, but the present invention is not limited to or restricted by the following working examples. In the examples, "parts" means parts by weight.

Working Example 1

An energy-ray curable resin composition that comprised 65 parts 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexyl carboxylate (epoxy equivalent weight: 131 to 143), 20 parts 1,4-butane diol diglycidyl ether (epoxy equivalent weight: 125 to 143), 15 parts of a thermoplastic saturated polyester resin (Vylon 500, a trade name, a product of Toyo Boseki Co., molecular weight: 20,000 to 25,000), 0.5 part of a silicone surface active agent, and 3 parts of a photopolymerization initiator PP-33 (a product of Asahi Denka Kogyo Co.) was diluted with 20 parts of an ethyl acetate solvent and applied to the surface of a magnetic tape-use polyester film (thickness: 12 μ) to form a 3 μ -thick film. The coated polyester film was run at a rate of 25 m/minute under a high-pressure mercury lamp (output: 80 W/cm, 4 KW) that was positioned 10 cm above the film and thus exposed to ultraviolet rays, thereby obtaining a coated polyester film with a coating film having excellent smoothness and adhesion. Next, on the surface of this coating-film layer, a thin metal cobalt layer was formed by vacuum vapor deposition. The resulting product had mirror gloss, and no peeling of the vapor deposited film occurred in a cellophane tape peeling test. On the other hand, with the aforesaid composition in which the thermoplastic saturated polyester resin was not compounded, coating-film peeling was observed when said polyester film was subjected to an adhesion test with the use of a cellophane tape.

Working Example 2

An energy-ray curable resin composition that comprised 30 parts 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexyl carboxylate (epoxy equivalent weight: 131 to 143), 40 parts bis(3,4-epoxycyclohexylmethyl) adipate (epoxy equivalent weight: 180 to 200), 20 parts 1,4-butane diol diglycidyl ether (epoxy equivalent weight: 125 to 143), 10 parts of a thermoplastic saturated polyester resin (Vylon 300, a trade name, a product of Toyo Boseki Co., molecular weight: 20,000 to 25,000), 1 part of a silicone surface active agent, and 3 parts of a photopolymerization initiator PP-33 (a product of Asahi Denka Kogyo Co.) was uniformly applied to the surface of a 120 μ -thick soft vinyl chloride film (the plasticizer content per 100 parts polyvinyl chloride: 40 parts) to a thickness of 4 μ . Next, the film was exposed to ultraviolet rays with the use of a high-pressure mercury lamp (output: 80 W/cm, 4 KW) by running the coated film at a position 10 cm below the lamp at a speed of 20 m/minute, thereby obtaining a coated soft vinyl chloride film whose cured coating film had excellent adhesion and flexibility. This coated vinyl film showed no fine cracks or peeling of the cured film even after it was subjected to a 500-hour durability test conducted with a Sunshine Super Long Run Weather Meter.

In a comparison test, the coated soft vinyl chloride film obtained by using said energy-ray curable resin composition that was prepared with no thermoplastic saturated polyester resin showed fine

cracks in the cured coating film when subjected to a weather test for 300 hours.

Working Example 3

An energy-ray curable resin composition that comprised 60 parts /129 trimethylolpropane triglycidyl ether (epoxy equivalent weight: 135 to 165), 30 parts 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexyl carboxylate (epoxy equivalent weight: 131 to 143), 10 parts of a thermoplastic saturated polyester resin (Vitel PE-200, a trade name, a product of Goodyear Co., molecular weight: 15,000 to 20,000), 0.5 part of a silicone surface active agent, and 3 parts of a photopolymerization initiator PP-33 (a product of Asahi Denka Kogyo Co.) was applied to the surface of a 100 μ -thick polycarbonate film to a thickness of 5 μ . The film was run at a rate of 10 m/minute under a high-pressure mercury lamp (output: 80 W/cm, 4 KW) that was positioned 10 cm above the film and thus exposed to ultraviolet rays, thereby obtaining a cured coating film. This coating film exhibited excellent adhesion in a cross-cut peeling test with a cellophane tape.

For comparison, a coating film prepared from said curable resin composition that contained no thermoplastic saturated polyester resin exhibited peeling in a cross-cut peeling test with a cellophane tape.

Working Example 4

An energy-ray curable resin composition that comprised 20 parts bisphenol A diglycidyl ether (epoxy equivalent weight: 180 to 200), 45 parts 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexyl carboxylate (epoxy

equivalent weight: 131 to 143), 20 parts 1,4-butane diol diglycidyl ether (epoxy equivalent weight: 125 to 143), 15 parts of a thermoplastic saturated polyester resin (Vylon GK-130, a trade name, a product of Toyo Boseki Co., molecular weight: 5,000 to 8,000), 0.5 part of a silicone surface active agent, and 4 parts of a photopolymerization initiator FC-508 (a product of Minnesota Mining And Manufacturing Co.) was diluted with 25 parts of an ethyl acetate solvent and applied to the surface of an aluminum sheet (0.2 mm) to a thickness of about 6 μ . The sheet was irradiated for 2 seconds under a high-pressure mercury lamp (output: 80 W/cm, 4 KW) that was positioned 15 cm above the sheet, thereby curing the coating film. The cured coating film formed on this aluminum sheet exhibited excellent cellophane tape-tested adhesion and bending processability.

In a comparison test, a coated aluminum sheet obtained by using said curable resin composition that contained no thermoplastic saturated polyether resin exhibited insufficient cellophane tape-tested adhesion.

Working Example 5

An energy-ray curable ink composition that comprised 70 parts 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexylmethyl carboxylate (epoxy equivalent weight: 131 to 143), 15 parts bisphenol A diglycidyl ether (epoxy equivalent weight: 450 to 500), 15 parts of a thermoplastic saturated polyester resin (Vylon 200, a trade name, a product of Toyo Boseki Co., molecular weight: 15,000 to 20,000), 12 parts of a blue

pigment Heliogen Blue (a product of BASF Co.), 2 parts of a silica-based additive, and 4 parts of a photopolymerization initiator FC-508 (a product of Minnesota Mining And Manufacturing Co.) was printed on a white coated acrylic plate. The plate was irradiated for 3 seconds under a high-pressure mercury lamp (output: 80 W/cm, 4 KW) that was positioned 15 cm above the plate, thereby drying the composition. This cured ink exhibited excellent adhesion to said coated plate in a cross-cut cellophane tape test.

In a comparison test, a printed coated plate obtained by using said energy-ray curable ink composition that contained no thermoplastic saturated polyether resin did not exhibit good adhesion when tested with a cellophane tape.